# Direct Measurements of Island Growth and Step-Edge Barriers in Colloidal Epitaxy

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**Epitaxial growth, a bottom-up self-assembly process for creating surface nano and microstructures, has been extensively studied in the context of atoms. This process however, is also a promising route to self-assemble nano and micron scale particles into microstructures with numerous technological applications. To determine if the well-established atomic epitaxial growth laws are applicable to the epitaxy of larger particles with attractive interactions, we investigate the nucleation and growth dynamics of colloidal crystal films with single-particle resolution. We show quantitatively that colloidal epitaxy obeys the same 2D island nucleation and growth laws that govern atomic epitaxy. Remarkably however, we find that in colloidal epitaxy, step-edge and corner barriers responsible for film morphology have a dynamic diffusive origin. This dynamic mechanism suggests new routes towards controlling film morphology during epitaxy.**

*Epitaxy* - the layer-by-layer growth of a crystalline film on a substrate (*1*) - plays a pivotal role in the fabrication of solid state and organic semiconductor devices, creation of strain relief

nanostructured arrays, and design of coatings with novel optical and mechanical properties (*2*). Understanding the microscopic details of the various growth processes at work continues to be a central focus of surface and materials science research (*1–7*). More recently this area of research has also branched out to include the self assembly of nano and micro scale particles into crystalline thin films for the purpose of creating tailor made meta materials and photonic band gap structures (***?***, ***?***, ***?***, *8*, *12*, *13*). While a variety of experimental techniques have been developed to study atomic homoepitaxy (*1*, *5*), these tools are not appropriate for investigating kinetic pathways in epitaxy of nano and micro scale particles. Without knowledge of these kinetic pathways, kinetic Monte Carlo (KMC) simulations cannot predict accurate growth laws. In fact, at present it is even unclear whether the same kinetic barriers that govern nucleation and growth in atomic systems also govern nano and micro particle epitaxy.

In this paper, we develop and integrate techniques in colloid science to study the epitaxy of micron scale particles with an attractive short-range depletion interaction (*14*). Since colloidal particles can be studied and manipulated at the single particle level, they are particularly well suited for investigating such phenomena. Our experiments show that the 2D growth laws for atoms and colloids are remarkably similar. In addition, we find that for colloids there exists an analogue of the atomic Ehrlich-Schwoebel barrier (ESB) - the energetic cost for moving a particle over a step edge or around an island corner (*15*, *16*). In atoms this barrier is thought to arise from long-range interparticle interactions. We show that in colloids, it originates from the diffusive nature of the particle dynamics. Nevertheless, this effective barrier leads to similar non-uniformities in the 2D and 3D island morphologies. These results demonstrate that key concepts derived from extensive studies on atomic epitaxial growth are directly applicable to film growth of larger scale particles. In addition, since colloids act as good model systems for studying statistical mechanics phenomena (*?*, *?*, *17–19*), concepts gleaned from these colloidal deposition experiments should offer insights into atomic and nanoparticle epitaxy.

Our systems consist of charge stabilized silica (or poly-styrene) colloids with diameter 1.0$\mu$m (or 1.3$\mu$m) and sodium polystyrene-sulfonate (or sodium carboxyl methyl cellulose) polymers with a radius of gyration of about $50$ nm. The polymers act as depletants that induce an effective attraction between the particles (*14*). Each colloidal epitaxy experiment consists of sedimenting particles onto a substrate at a fixed flux $F$. To make contact with atomic epitaxy experiments, a single crystalline colloidal monolayer, formed by binding particles to a lithographically patterned template, is used as the substrate (Fig. 1) (*20*). The sedimented particles perform a 2D-random walk on the substrate by thermally activated hops and coalesce into crystalline islands (movie S1). We find that the monomer surface diffusion constant $D$ is about $0.01\mu\text{m}^2/s$ which is 100 times smaller than the two-dimensional diffusion constant for a free particle in liquid (supporting online text). This decrease arises from depletion induced bonds with the underlying substrate that create an energetic barrier that has to be overcome for particles to hop from one interstitial site to another. The ratio of $D/F$ determines the size of the region explored by the particle before it meets another particle, island, or step-edge and is a key parameter that governs thin film growth (*1,5*).

In order to compare epitaxy of colloids and atoms, a significant overlap in $D/F$ values is essential. The expression for $D$ has an activated form $D = D_0 \exp(-U/k_bT)$ where $D_0$ is the attempt frequency and $U$ is the activation barrier (*1,5*). In colloid experiments, $U$ can be made arbitrarily small by tuning the depletant concentration. Thus, even though $D_0$ is approximately $10^8$ times smaller than in atoms, by careful control over the deposition flux, $D/F$ can be tuned from $10^{-1}$ to $10^4$. For atomic deposition $10^{-1} < D/F < 10^9$ (*5*). This significant overlap in $D/F$ values allows for quantitative comparison of the mechanisms governing film growth in these two systems.

We show snapshots of nucleation and island growth on a square lattice with $D/F = 1352$ in Figs. 2a1-2a4. In our experiments dimers act as stable nucleation sites. Therefore, we

define an island as a cluster equal to or greater than two particles. With time, we observe nucleation of numerous disconnected islands that grow and eventually coalesce to form a single monolayer. The number of disconnected islands per unit area, $n$, versus area fraction of islands, $\Theta$, for this $D/F$ ratio is shown by the solid blue squares in Fig. 2b. Initially, the monomer density on the substrate rises and leads to a linear increase in $n$ (Figs. 2a1 and 2a2, movie S2). At later times the island density reaches a critical density $n_c$ and begins to drop since arriving monomers diffuse to nearby islands before encountering other monomers. By varying the substrate symmetry (movie S3), depletant concentration, and bulk colloid volume fraction, we tune $D$ and $F$ independently. This allows for conducting epitaxy experiments at different $D/F$ ratios (Fig. 2b).

In Fig. 2c we compare the measured $n_c$ versus $D/F$ for our colloid experiments (solid symbols) with those from atomic experiments (inverted hollow triangles) (*21*), atomic KMC simulations (hollow squares) (*5*), rate equation with post deposition mobility (brown line) and the rate equation for stable islands (green line) (*21*). Remarkably, we find excellent quantitative agreement between the colloid and atom data. At high $D/F$ ratio our data approaches the $n_c \propto D/F^{-1/3}$ scaling predicted by classical nucleation theory for systems where dimers form stable islands (*3*,*5*). At $D/F \approx 50$, $n_c$ reaches a maximum and decreases for lower $D/F$ ratios since diffusion becomes slow and fewer islands nucleate and grow during deposition (*21*, *22*). We even find that the measured maximum value for $n_c$ agrees with the atomic experiments and the theoretical prediction for systems with stable dimer islands. These data indicate that scaling laws relevant for atoms carry over to 2D film growth of larger scale particles with attractive interactions.

In addition to island growth, controlling island morphology is of central importance in the growth of high quality crystalline films (*1*). In atoms, the fundamental parameters that determine island morphology in 2D and 3D are the Ehrlich-Schwoebel corner and step-edge kinetic

barriers (*1,15,16,23*). Such barriers are thought to arise from the interactions between the atoms and their neighbors. Specifically, as an atom hops from one interstitial site to another on the same island, it must break bonds with its nearest neighbors and form bonds at the new site. Since a new bond is able to form as the old one is broken, the energetic cost for going through the lower coordination number state during the hop is minimal. Since the distances between sites straddling a step-edge or corner are longer than those between other adjacent sites on the island, the energetic barriers for hopping over step-edges and corners are substantially larger (Figs. 3a and 3b). Since depletion interactions in our experiments are very short-ranged, extending to only a twentieth of the particle diameter, these arguments do not hold for our colloidal system. Nevertheless, in our experiments on colloids we do find evidence of such barriers. For example, we observe nucleation on top of islands even when the separation between them is larger than the average island size, a phenomenon that in atomic epitaxy is associated with an ESB (Figs. 3c and 3d) (*1*).

In order to unambiguously determine whether a step-edge barrier exists for colloids with short ranged interactions, it is necessary to compare hopping dynamics of particles moving from one island interstitial site to another with those of particles descending island step-edges. To quantify these dynamics, we use holographic optical tweezers (Arryx Inc.) (*24*) to place individual colloids on islands consisting of different numbers of particles (supporting online text)(movie S4). We then turn the tweezers off and track the colloids as they move to different island sites (movie S5 and S6). Particle trajectories of 180s duration are shown for a large triangular island, where the diffusing colloid explores only interior interstitial sites (Fig. 3e), and a three particle triangular island, where all excursions are over step-edges (Fig. 3f). The trajectories show that island step-edges significantly confine the space explored by a diffusing monomer. By repeating these experiments 600 times, we quantify the difference in residence times between interstitial sites away from step-edges and those at a step-edge. As shown in

Fig. 3g, interstitial residence time for a monomer on a large island peaked at $\tau_i \approx 8.2$s while the residence time for a colloid on a three particle island peaked at $\tau_s \approx 22.5$s. This threefold increase clearly indicates that despite the short-range nature of the particle interactions, step-edge barriers also exist in colloidal epitaxy.

As the particle trajectories in Figs. 3e and 3f show, once a bond is broken with the underlying lattice, colloid monomers predominantly diffuse along local 1D trajectories corresponding to the valleys formed by the underlying particles. Thus the process of moving from one site to another can be modeled as a 1D random walk between partially absorbing boundaries (*25*). Since particles on islands with triangular symmetry must diffuse twice as far to descend a step-edge, the diffusion time and the probability of returning to the origin (*26*) and reforming the original bonds increases (Fig. 3h). In the weak interaction limit the diffusion time dominates so that it takes four times as long to descend a step-edge than to move to a neighboring site on the island interior. In the strong interaction limit, the bond breaking time dominates. Since the probability of returning to the origin in a 1D random walk grows linearly with the end-to-end distance (*27*), it would take particles on triangular islands twice as long to descend a step-edge than to move to a neighboring site on the island interior. The ratio of residence times in our measurements is $\approx$ 2.7 indicating that both the diffusion and bond breaking time scales contribute to the observed barriers. Furthermore, this 1D diffusion model suggests that residence times on island sites should increase with the number of descent pathways, $p$ as $\tau = \tau_i/3 * (3 - p) + \tau_s/3 * p$. To test this prediction we conducted 100 independent experiments with a total of 1089 monomer hops on a triangular island where different perimeter sites have a different number of descent pathways (movie S7). Figs. 3i and 3j show that the residence times are in excellent agreement with these predictions.

Collectively, these results indicate that epitaxy in colloidal systems is remarkably similar to epitaxy in atoms. We have shown that as with atoms the ratio of $D/F$ dictates the 2D

growth laws. In addition, we have uncovered a new dynamic mechanism that leads to step-edge and corner barriers even in systems with short-range interactions. Implementing techniques that use gravity or electromagnetic fields to bias the diffusion of particles down step-edges would lower the step-edge barrier and lead to significantly smoother films. Such techniques could also be used to tune barriers in nanoparticle and molecular systems. The powerful array of tools that we have brought together to investigate colloidal epitaxy may also be helpful in elucidating mechanisms that have proved difficult to study in atoms such as dynamic stress relaxation mechanisms in strained layer heteroepitaxy (*6*). Finally, given the rapid advances in synthesizing micro and nano scale colloidal particles with directional interactions (*28*) and anisotropic shapes (*29*), we expect that future epitaxy experiments with such particles will lead to a valuable exchange of ideas between the fields of microparticle, nanoparticle and atomic epitaxy.

# References and Notes


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**Supporting Online Material**

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Materials and Methods

Figs. S1

Movie S1 to S7

**Fig. 1.** Confocal micrographs of silica colloid monolayers. The particles are seen as dark circles in a bright fluorescent background. (a) Triangular lattice with lattice spacing $1.05\mu$m. (b) Square lattice with lattice spacing $1.04\mu$m.

**Fig. 2.** (a) Four images from an island nucleation and growth experiment on a square template with $D/F = 1352$. (b) Island density measurements at various $D/F$ values for square and triangular lattices. Square lattice data for $D/F = 1352$ (■), $D/F = 116$ (□), $D/F = 5.7$ (□). Triangular lattice data for $D/F = 4238$ (△), $D/F = 130.5$ (△). (c) $n_c$ versus $D/F$ for atomic deposition experiments (∇); for KMC simulations (□) (from (*5*)); rate equation with post-deposition mobility is represented by the brown line; rate equation for stable islands is represented by the green line (from (*21, 22*)). The colloid epitaxy experiments with silica particles on the square lattice are shown by (■), while those on the triangular lattice are shown by (▲). Experiments with polystyrene particles on a square lattice are shown by (♦). The data corresponds to systems where dimers form stable island nuclei.

**Fig. 3.** (a) Schematic of adatom diffusing near an island step-edge. (b) Energy landscape for atoms near a step-edge. (c) Image of islands growing on the monolayer substrate. (d) Image of islands nucleating on top of islands shown in (c) (red outline). The separation between islands in (c) is $\approx 8.0$ lattice constants while the radius of the islands in (d) is $\approx 2.5$ lattice constants. Such features in atomic systems are associated with a step-edge barrier. (e) Polystyrene colloid diffusing on a colloidal monolayer with triangular symmetry. The trajectory of the colloid during a 180 s interval is shown in red with green dots. (f) Trajectory of a polystyrene colloid diffusing on a 3-particle island over a 180 s duration. (g) Interstitial residence time distribution for a colloidal particle diffusing on a monolayer (top panel) and for a particle diffusing on a 3-particle island (bottom panel). (h) Energy landscape for colloids near a step-edge. (i) Interstitial residence time distribution on a 15-particle island. Color bars indicate residence time. (j) Experimental residence times (symbols) versus number of descent pathways. Linear fit to data

(red line). 95% confidence intervals (dashed lines).

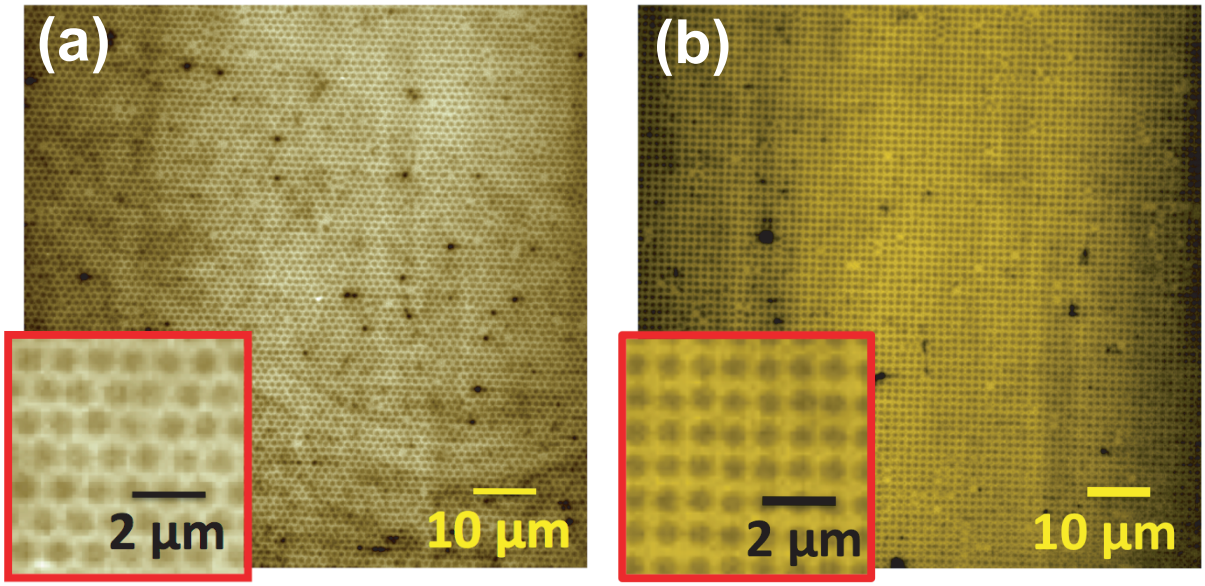


**Fig. 1**

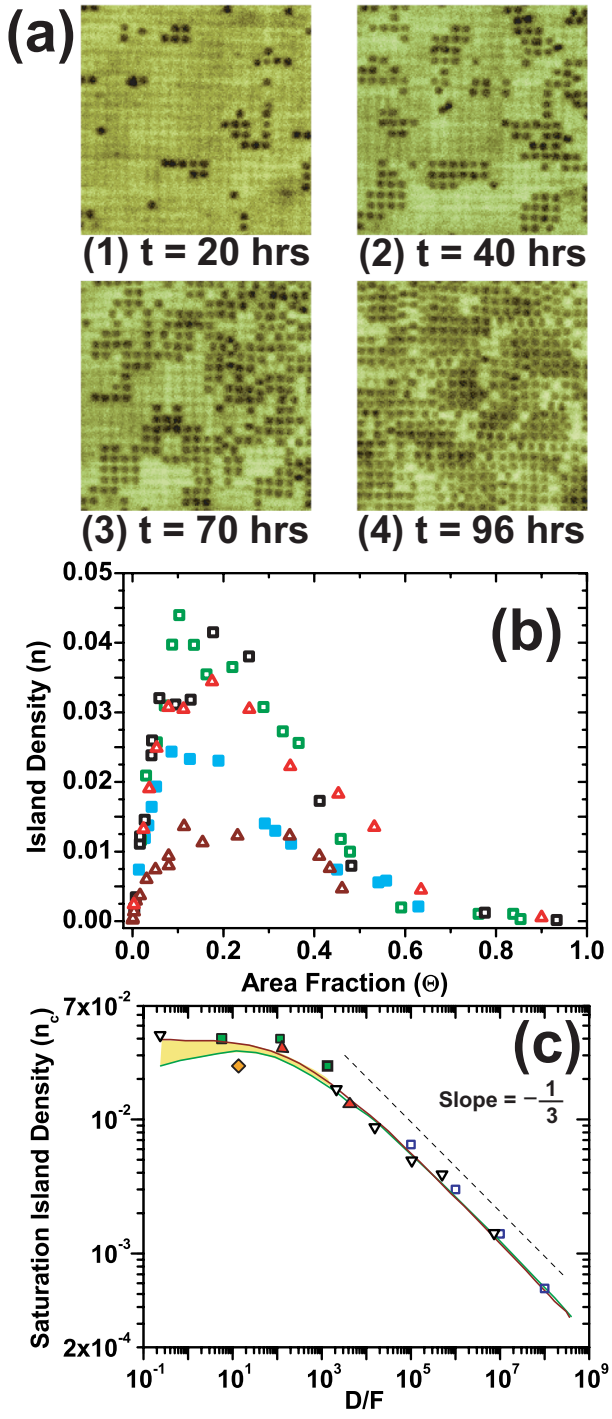
(a)
(1) t = 20 hrs
(2) t = 40 hrs
(3) t = 70 hrs
(4) t = 96 hrs
(b)
Island Density (n)
0.05
0.04
0.03
0.02
0.01
0.00
0.0
0.2
0.4
0.6
0.8
1.0
Area Fraction (Θ)
(c)
Saturation Island Density (n_c)
7x10^-2
10^-2
10^-3
2x10^-4
10^-1
10^1
10^3
10^5
10^7
10^9
D/F
Slope = −1/3

**Fig. 2**

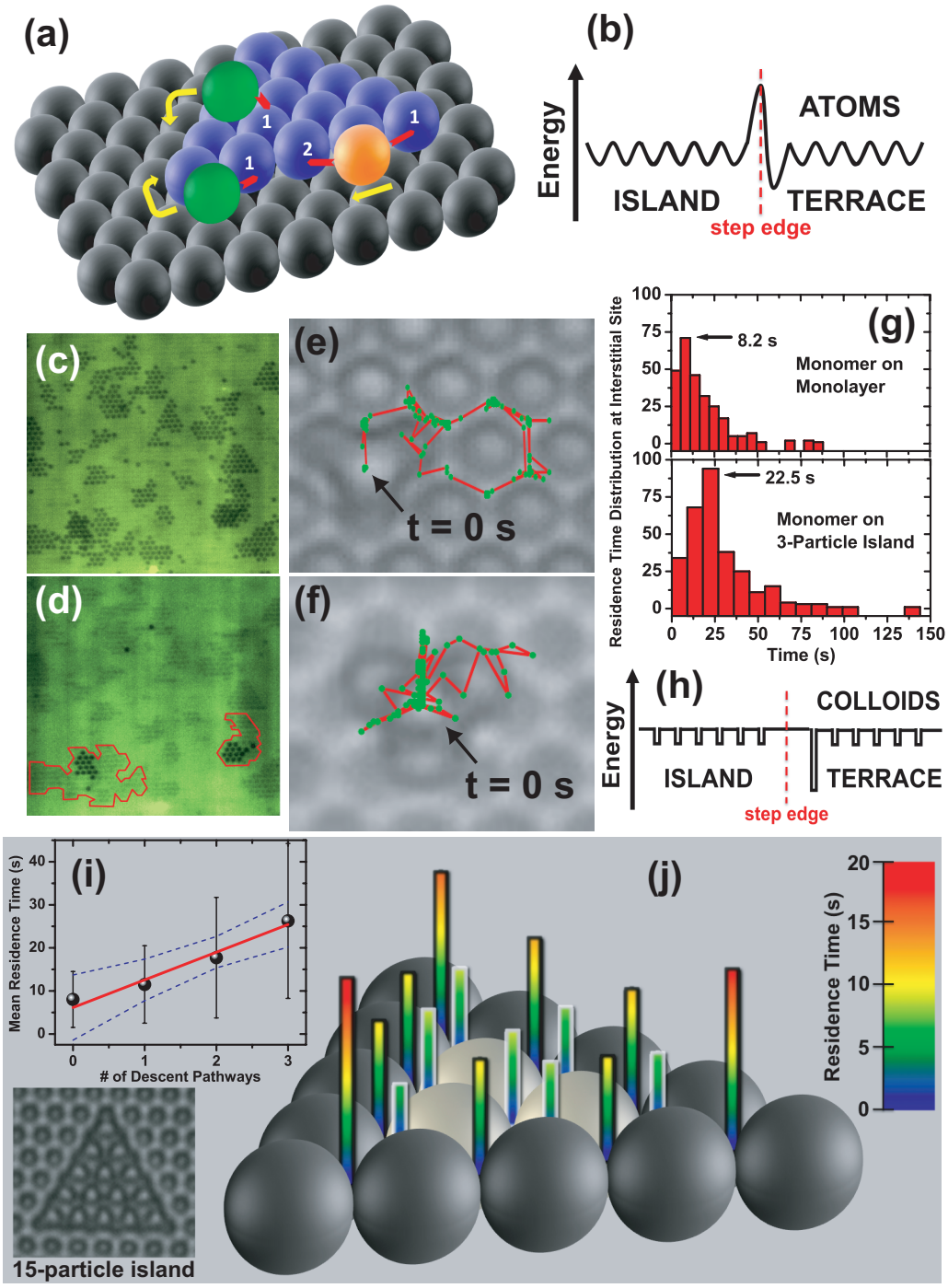
(a)
1
1
2
1
(b)
Energy
ATOMS
ISLAND
TERRACE
step edge
(c)
(d)
(e)
t = 0 s
(f)
t = 0 s
(g)
Residence Time Distribution at Interstitial Site
8.2 s
Monomer on
Monolayer
22.5 s
Monomer on
3-Particle Island
Time (s)
(h)
Energy
COLLOIDS
ISLAND
TERRACE
step edge
(i)
Mean Residence Time (s)
# of Descent Pathways
15-particle island
(j)
Residence Time (s)

**Fig. 3**

**Supporting Online Material**

*Fabrication of colloid monolayers*

To fabricate our substrates we first lithographically pattern an array of 0.96$\mu$m (or 1.26$\mu$m) diameter holes in a 500 nm thick polymethylmethacrylate layer that we spin coat on an Indium-Tin Oxide coated coverslip. This conducting coverslip acts as the bottom electrode of an electrophoretic flow cell as shown in Fig. S1. The flow cell is filled with a suspension of silica particles that does not contain any depletant. When approximately 20 layers have sedimented, the negatively charged particles are pushed into the holes. Applying a DC electric field of about 14 kV/m between the top and bottom electrodes permanently binds the silica particles to the Indium-Tin Oxide layer at the bottom of the holes. Simultaneously, the cell is flushed with pure de-ionized water and all layers except the first are washed away. Figure 1a and 1b show confocal micrographs of a typical monolayer of colloids pinned to a triangular lattice and square lattice respectively.

*Measurement of diffusion constant*

To determine $D$ we track (*1*) individual silica particles diffusing on these colloidal monolayers in the presence of our depletant (movie S1). We measure the mean-squared displacement $\Delta r^2$ as a function of time $t$, while carefully ignoring particles with intralayer interactions (particle-particle and/or particle-island). We find that $\Delta r^2 \propto t$ and use the two-dimensional Stokes-Einstein relation to determine $D$.

*Monolayer and island fabrication using holographic optical tweezers*

To make small monolayers and islands for our step-edge barrier measurements, we use the holographic optical tweezers to trap and place individual particles into the lithographically patterned holes in the presence of a depletant (movie S4). The islands are assembled on the colloidal monolayer using a similar procedure. The overlap volume that is freed up when a particle interacts with a hole is larger than the overlap volume freed up when a particle interacts with

another particle. Thus the depletion interaction between the first layer of particles and the holes is significantly stronger compared to the depletion interaction between particles on subsequent layers with the layer below.

## References and Notes

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**Fig. S1.** Schematic of the flow cell used to make the substrates in our experiments. The pattern of holes is made on the conducting side of an ITO coated coverslip. The monolayers are formed for a typical electrode separation of $\approx 175\mu$m. This height was increased to achieve complete thin film coverage in experiments performed at a low $F$. We typically form monolayers with greater than $99\%$ coverage.

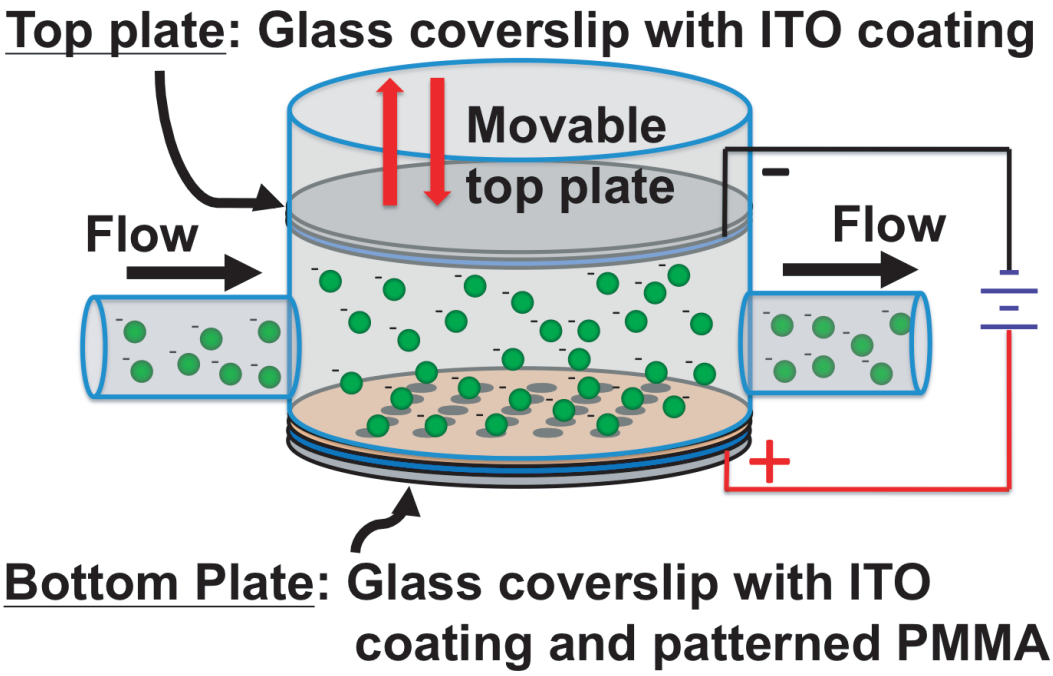
Top plate: Glass coverslip with ITO coating
Movable
top plate
Flow
Flow
−
+
Bottom Plate: Glass coverslip with ITO
coating and patterned PMMA

**Fig. S1**